

Diffusion in multicomponent systems: a free energy approach

Simon Emmanuel, Andrea Cortis, Brian Berkowitz *

Department of Environmental Sciences and Energy Research, Weizmann Institute of Science, Herzl St. 200, 76100 Rehovot, Israel

Received 19 November 2003; accepted 17 March 2004

Available online 2 April 2004

Abstract

This work examines diffusion in ternary non-ideal systems and derives coupled non-linear equations based on a non-equilibrium thermodynamic approach in which an explicit expression for the free energy is substituted into standard diffusion equations. For ideal solutions, the equations employ four mobility parameters (M_{aa} , M_{ab} , M_{ba} , and M_{bb}), and uphill diffusion is predicted for certain initial conditions and combinations of mobilities. For the more complex case of ternary Simple Mixtures, two non-ideality parameters (χ_{ac} and χ_{bc}) that are directly related to the excess free energy of mixing are introduced. The solution of the equations is carried out by means of two different numerical schemes: (1) spectral collocation and (2) finite element. An error minimization technique is coupled with the spectral collocation method and applied to diffusional profiles to extract the M and χ parameters. The model satisfactorily reproduces diffusional profiles from published data for silicate melts. Further improvements in numerical and experimental techniques are then suggested.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Uphill diffusion; Ternary mixtures; Non-ideal solutions; Silicate melts

1. Introduction

Diffusion in multicomponent systems plays an important role in numerous natural and industrial processes, from magmatic and metamorphic petrology, to the production of polymers and metal alloys. Often complicating attempts to model the diffusional process is a phenomenon called “uphill diffusion” in which diffusion of at least one of the components occurs in the direction counter to that of its concentration gradient. This phenomenon was first suggested in the theoretical study of Toor [1] and subsequently demonstrated experimentally in numerous works.

To illustrate this behavior, it is instructive to consider the experiment conducted by Oishi et al. [2] (Fig. 1) in which a ternary diffusion couple was constructed with initial concentration gradients in the Al_2O_3 and SiO_2 components and a uniform CaO concentration. From a

simple Fickian approach to diffusion, it might be expected that as no initial CaO gradient existed, no change in its concentration would be observed during the experiment. However, after termination of the experimental run, pronounced uphill diffusion was nevertheless evident in the CaO component. Such experiments have demonstrated that the diffusion of one component is often strongly coupled to that of the other components in the system. Studies examining silica melts and glasses [2–8] and magmatic and metamorphic minerals [9–12] indicate that uphill diffusion is likely to be a significant factor in determining the evolution of these high temperature systems.

While a number of different approaches have been proposed for the treatment of diffusion in multicomponent systems, such as relaxation velocity modeling [13], irreversible thermodynamic analysis [14,15], the modified binary diffusion model [16], the Maxwell–Stefan formulation, e.g. [17], and the “flux reversal” model [18], perhaps the most widely used method is that of “ D matrix modeling” [19]. In this approach, Fick’s law is modified so that the flux of each component is determined not only by its own gradient, but by the gradients

* Corresponding author. Tel.: +97289342098; fax: +97289344124.

E-mail addresses: simon.emmanuel@weizmann.ac.il (S. Emmanuel), andrea.cortis@weizmann.ac.il (A. Cortis), brian.berkowitz@weizmann.ac.il (B. Berkowitz).

Nomenclature

List of symbols

a, b, c	chemical components
n	number of moles (mol)
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
G	generalized free energy ($\text{J mol}^{-1}/(RT)$)
G^{ideal}	ideal free energy of mixing ($\text{J mol}^{-1}/(RT)$)
G^{mix}	free energy of mixing ($\text{J mol}^{-1}/(RT)$)
G^{xs}	excess free energy of mixing ($\text{J mol}^{-1}/(RT)$)
J	normalized molar flux ($\text{mol m}^{-2} \text{s}^{-1}/(\text{mol m}^{-3})$)

M	mobility coefficient ($\text{m}^2 \text{s}^{-1}$)
\mathcal{M}	memory function (s^{-1})
R	universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
T	temperature (K)

Greek symbols

μ	chemical potential ($\text{J mol}^{-1}/(RT)$)
ϕ	mole fraction
χ	non-ideality parameter ($\text{J mol}^{-1}/(RT)$)

of the other components as well. For a ternary system two coupled equations for the fluxes of two of the three components, say a and b , can be written in the form [20]

$$J_a = -(D_{aa}\nabla\phi_a + D_{ab}\nabla\phi_b), \quad (1a)$$

$$J_b = -(D_{ba}\nabla\phi_a + D_{bb}\nabla\phi_b), \quad (1b)$$

where J is a mole density normalized flux (dimensions of $[\text{LT}^{-1}]$), ϕ_i is a mole fraction ($\sum \phi_i = 1$), D_{aa} and D_{bb} are

the “intrinsic” diffusion coefficients, and D_{ab} and D_{ba} are “mutual” diffusion coefficients. While the D matrix method is attractive due to its relative simplicity, determining the values of the coefficients for different systems, such as silicate melts, involve both theoretical and practical difficulties, e.g. [6,7,21,22].

One of the main problems associated with D matrix modeling is the uncertainty related to the compositional dependence of the coefficients. While a strong relationship between the concentration of components and the magnitudes of the coefficients has been demonstrated experimentally in silicate systems [8], very little is typically known concerning how these coefficients change with physical parameters, such as concentration, temperature, and pressure. Thus, in real systems where compositional changes have the potential to be relatively large, D coefficients determined in a specific concentration range may have a limited predictive capability.

In addition to these limitations of the D matrix method, there are often difficulties in reproducing experimentally measured profiles. For instance, using the D matrix approach, Kress and Ghiorso [21] were unsuccessful in reproducing the second order features observed in multicomponent diffusion experiments with silica glasses. As a result, they concluded that alternative models, possibly based on free energy rather than concentration gradients, are required in order to fully capture the behavior of such complex systems. Although more computationally demanding, models that describe diffusion in terms of free energy gradients have the potential to more accurately match experimental data and predict system behavior.

In this paper, the efficacy of one possible free energy approach is explored and its application to real multicomponent systems is examined. Non-equilibrium thermodynamic theory and a specific expression for the free energy of mixing are used as a basis to develop coupled non-linear equations governing diffusion in ternary systems (Section 2). These equations are then solved numerically (Section 3) and compared to data from diffusion experiments (Section 4). In Section 5, the re-

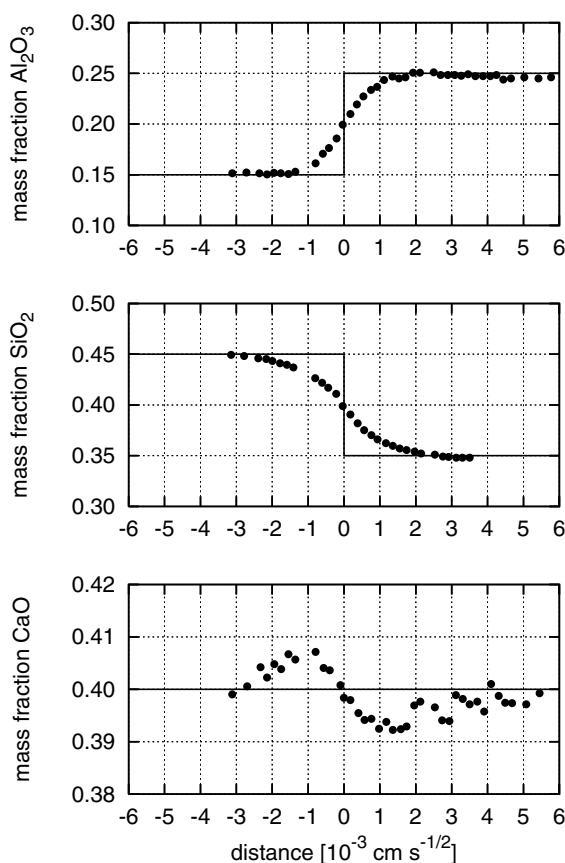


Fig. 1. Concentration profiles for a CaO–Al₂O₃–SiO₂ liquid state silicate diffusion couple. Initial concentrations are indicated by solid lines while concentrations measured after 11 min are represented by markers. The horizontal distance axis has been normalized by \sqrt{t} . Data from Oishi et al. [2].

sults are discussed and implications for future theoretical, numerical, and experimental studies are examined.

2. Theory

As discussed in the previous section, uphill diffusion often occurs in multicomponent systems in which concentration gradients exist. In addition to being associated with these systems, uphill diffusion is also a typical feature of phase separation processes, in which initially homogeneous mixtures may separate into distinct phases as a result of changes in system parameters.

In order to describe phase separation in a binary system, Cahn and Hilliard [23] introduced an additional term, describing the effect of interfacial energy, into the expression for the total free energy of the system. Subsequent theoretical efforts examining phase separation in binary and ternary systems have generally focused on developing expressions that describe the redistribution of free energy with time within such systems. Motivated by the study of Nauman and He [24] which examined phase separation involving multiple components, an alternative approach to multicomponent diffusion in single-phase systems is presented here. Although limited to three component systems, the derivation can be extended to deal with a greater number of components with relative ease.

Before developing expressions for the mass fluxes in ternary systems, the “generalized” expression for the chemical potential, μ , of each of the three components, a , b , and c , will be defined as [24]

$$\begin{aligned}\mu_a &= \left(\frac{\delta nG}{\delta n_a} \right)_{T,P,n_b,n_c}, & \mu_b &= \left(\frac{\delta nG}{\delta n_b} \right)_{T,P,n_a,n_c}, \\ \mu_c &= \left(\frac{\delta nG}{\delta n_c} \right)_{T,P,n_a,n_b},\end{aligned}\quad (2)$$

where $n_a + n_b + n_c = n$ is the total number of moles, and G is the generalized free energy of the system. The δ notation represents the variational partial derivative defined as

$$\frac{\delta f}{\delta g} = \left(\frac{\partial f}{\partial g} \right) - \nabla \cdot \left(\frac{\partial f}{\partial \nabla g} \right) \quad (3)$$

in which the derivative of f with respect to g is expressed as a function of both g and the gradient of g . While the concentration gradients are not generally thought to contribute to the chemical potentials in non-phase separating systems, an assumption that reduces the variational derivative to the standard partial derivative, such formalism is crucial for the treatment of mass transfer during phase separation, and will be retained for the sake of generality. In the following development, the chemical potentials have been normalized by RT (R is the gas constant and T is temperature).

By combining the definitions in (2) and (3) with classical thermodynamic theory, two independent expressions can be obtained for the components a and b [25]

$$\mu_a = G - \phi_b \left(\frac{\delta G}{\delta \phi_b} \right)_{\phi_c} - \phi_c \left(\frac{\delta G}{\delta \phi_c} \right)_{\phi_b}, \quad (4a)$$

$$\mu_b = G - \phi_a \left(\frac{\delta G}{\delta \phi_a} \right)_{\phi_c} - \phi_c \left(\frac{\delta G}{\delta \phi_c} \right)_{\phi_a}. \quad (4b)$$

Importantly, these expressions satisfy Euler’s theorem

$$\phi_a \mu_a + \phi_b \mu_b + \phi_c \mu_c = G \quad (5)$$

and the Gibbs–Duhem equation

$$\phi_a \nabla \mu_a + \phi_b \nabla \mu_b + \phi_c \nabla \mu_c = 0. \quad (6)$$

For a non-phase separating system, the generalized free energy, G , reduces to the free energy of mixing, G^{mix} , and it can be shown that the gradients of the chemical potentials are then given by the expressions (see Appendix A)

$$\nabla \mu_a = -\phi_b \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} - \phi_c \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b} \quad (7a)$$

and

$$\nabla \mu_b = -\phi_a \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_a} \right)_{\phi_c} - \phi_c \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_a}. \quad (7b)$$

By substituting ϕ_c with $1 - \phi_a - \phi_b$ the following is obtained:

$$\nabla \mu_a = -\phi_b \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_a} + (1 - \phi_a - \phi_b) \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_a} \right)_{\phi_b} \quad (8a)$$

and

$$\nabla \mu_b = -\phi_a \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_a} \right)_{\phi_b} + (1 - \phi_a - \phi_b) \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_a}. \quad (8b)$$

Furthermore, (8) can be rewritten in order to express the chemical potential gradients as functions of the concentration gradients

$$\begin{aligned}\nabla \mu_a &= -\phi_b \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b + (1 - \phi_a - \phi_b) \\ &\quad \times \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a\end{aligned} \quad (9a)$$

and

$$\begin{aligned} \nabla \mu_b = & -\phi_a \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a + (1 - \phi_a - \phi_b) \\ & \times \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b. \end{aligned} \quad (9b)$$

If it is assumed that the driving force for diffusion of a given species is only dependent on the chemical potential gradients of the two independent components, a and b , the expressions for the fluxes are given by [26]

$$J_a = -[M_{aa}\phi_a \nabla \mu_a + M_{ab}\phi_a \nabla \mu_b], \quad (10a)$$

$$J_b = -[M_{ba}\phi_b \nabla \mu_a + M_{bb}\phi_b \nabla \mu_b], \quad (10b)$$

where the M coefficients are mobility terms or diffusivities [L^2T^{-1}]. The parameters M_{aa} and M_{bb} must necessarily be positive, although M_{ab} and M_{ba} may be either positive or negative. The magnitudes of the cross terms reflect the relative degree of coupling between the two fluxes. The substitution of (9) into (10) yields

$$\begin{aligned} J_a = & -M_{aa}\phi_a \left[(1 - \phi_a - \phi_b) \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a \right. \\ & \left. - \phi_b \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b \right] \\ & + M_{ab}\phi_a \left[\phi_a \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a - (1 - \phi_a - \phi_b) \right. \\ & \left. \times \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b \right] \end{aligned} \quad (11a)$$

and

$$\begin{aligned} J_b = & M_{bb}\phi_b \left[\phi_a \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a - (1 - \phi_a - \phi_b) \right. \\ & \times \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b \left. \right] - M_{ba}\phi_b \left[(1 - \phi_a - \phi_b) \right. \\ & \times \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a - \phi_b \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b \left. \right]. \end{aligned} \quad (11b)$$

Rearranging, it follows that

$$\begin{aligned} J_a = & [M_{ab}\phi_a^2 - M_{aa}\phi_a(1 - \phi_a - \phi_b)] \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a \\ & + [M_{aa}\phi_a\phi_b - M_{ab}\phi_a(1 - \phi_a - \phi_b)] \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b \end{aligned} \quad (12a)$$

and

$$\begin{aligned} J_b = & [M_{bb}\phi_a\phi_b - M_{ba}\phi_b(1 - \phi_a - \phi_b)] \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} \nabla \phi_a \\ & + [M_{ba}\phi_b^2 - M_{bb}\phi_b(1 - \phi_a - \phi_b)] \left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} \nabla \phi_b. \end{aligned} \quad (12b)$$

It is clear from (12) that precise knowledge of G^{mix} as a function of composition is crucial in order to determine mass transport in diffusive ternary systems. In such systems, the free energy of mixing is given by the expression

$$G^{\text{mix}} = G^{\text{ideal}} + G^{\text{xs}}, \quad (13)$$

where G^{ideal} is the entropic contribution to the free energy characteristic of ideal systems such that

$$\begin{aligned} G^{\text{ideal}} = & \phi_a \ln \phi_a + \phi_b \ln \phi_b + (1 - \phi_a - \phi_b) \\ & \times \ln(1 - \phi_a - \phi_b) \end{aligned} \quad (14)$$

and G^{xs} is the enthalpic contribution for non-ideal systems.

In non-ideal systems (i.e., $G^{\text{xs}} \neq 0$), a suitable expression for G^{xs} may be obtained from the Simple Mixture model for three components [25,27,28] yielding

$$\begin{aligned} G^{\text{xs}} = & \chi_{ab}\phi_a\phi_b + \chi_{ac}\phi_a(1 - \phi_a - \phi_b) \\ & + \chi_{bc}\phi_b(1 - \phi_a - \phi_b). \end{aligned} \quad (15)$$

In this formulation χ_{ab} , χ_{bc} , and χ_{ac} are thermodynamic parameters that account for non-ideal interactions between the different species. These parameters may be either positive or negative, reflecting the endothermic or exothermic nature of the mixing process, respectively. Values for χ in silicate minerals are generally found to be temperature dependent, possessing either positive or negative values with a typical range of 0–2, although higher values have been reported [28]. Significantly, the ternary Simple Mixture model has often been used to describe geological systems [28].

Adopting the expressions in (14) and (15), the second partial derivatives of G^{mix} with respect to composition are thus given by

$$\left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_a^2} \right)_{\phi_b} = \frac{1 - \phi_b - 2\chi_{ac}\phi_a(1 - \phi_a - \phi_b)}{\phi_a(1 - \phi_a - \phi_b)} \quad (16a)$$

and

$$\left(\frac{\partial^2 G^{\text{mix}}}{\partial \phi_b^2} \right)_{\phi_a} = \frac{1 - \phi_a - 2\chi_{bc}\phi_b(1 - \phi_a - \phi_b)}{\phi_b(1 - \phi_a - \phi_b)}. \quad (16b)$$

By substituting (16) into (11) and simplifying, the full expressions for the fluxes J_a and J_b become

$$J_a = L_{aa}\nabla \phi_a + L_{ab}\nabla \phi_b \quad (17a)$$

and

$$J_b = L_{ba} \nabla \phi_a + L_{bb} \nabla \phi_b, \quad (17b)$$

where

$$L_{aa} \equiv [M_{ab}\phi_a - M_{aa}(1 - \phi_a - \phi_b)] \times \left(\frac{1 - \phi_b - 2\chi_{ac}\phi_a(1 - \phi_a - \phi_b)}{(1 - \phi_a - \phi_b)} \right), \quad (18a)$$

$$L_{ab} \equiv [M_{aa}\phi_a\phi_b - M_{ab}\phi_a(1 - \phi_a - \phi_b)] \times \left(\frac{1 - \phi_a - 2\chi_{bc}\phi_b(1 - \phi_a - \phi_b)}{\phi_b(1 - \phi_a - \phi_b)} \right), \quad (18b)$$

$$L_{ba} \equiv [M_{bb}\phi_a\phi_b - M_{ba}\phi_b(1 - \phi_a - \phi_b)] \times \left(\frac{1 - \phi_b - 2\chi_{ac}\phi_a(1 - \phi_a - \phi_b)}{\phi_a(1 - \phi_a - \phi_b)} \right), \quad (18c)$$

$$L_{bb} \equiv [M_{ba}\phi_b - M_{bb}(1 - \phi_a - \phi_b)] \times \left(\frac{1 - \phi_a - 2\chi_{bc}\phi_b(1 - \phi_a - \phi_b)}{(1 - \phi_a - \phi_b)} \right). \quad (18d)$$

Assuming a system in which density remains constant, the continuity equations for the mole fractions are defined as

$$\frac{\partial \phi_a}{\partial t} = -\nabla \cdot J_a \quad (19a)$$

and

$$\frac{\partial \phi_b}{\partial t} = -\nabla \cdot J_b. \quad (19b)$$

Thus, the non-linear system of partial differential equations in (17)–(19) describe ternary diffusion in Simple Mixture solutions in terms of four mobility and two thermodynamic parameters.

From a comparison of (1) with (17), it can be seen that the flux expressions developed here differ from the D matrix model in a number of ways. One of the most obvious differences between the two models is apparent from an examination of the L and D matrices. Significantly, the free energy approach replaces the constant D coefficients with expressions that are explicitly concentration dependent. Thus, the mobility parameters, M , are expected to be less influenced by concentration than the D coefficients.

The χ parameters introduce additional degrees of freedom which can resolve differences between theory and experimental observations. Notably, the χ parameters of the free energy model can be used to constrain thermodynamic values, such as the excess free energy of mixing, an approach similar to that suggested by Chakraborty [29]. Importantly, these thermodynamic parameters are crucial in understanding a variety of processes, including mineral crystallization in magmatic and metamorphic systems. Thus, in addition to potentially presenting a more accurate description of multi-component systems, the model could be applied to diffusional data to constrain thermodynamic parameters

which prove impractical to obtain by alternative methods.

3. Numerical analysis

In order to solve the diffusion equations in (19) for 1D systems, two different numerical schemes were developed and compared. One scheme implemented a finite element method using the FEMLAB[®] software package, while the other was based on a spectral collocation method [30,31]. In the finite element scheme, a mesh consisting of 240 Lagrange quadratic elements was adopted, together with a time dependent fifth order solver based on the numerical differentiation formulas (*ode15s* function in MATLAB[®]). Increasing the mesh density was found to have no significant effect on the solution. Although stable solutions were usually obtained using this method, it was noted that for certain combinations of initial conditions and values of M and χ , numerical instabilities became dominant preventing

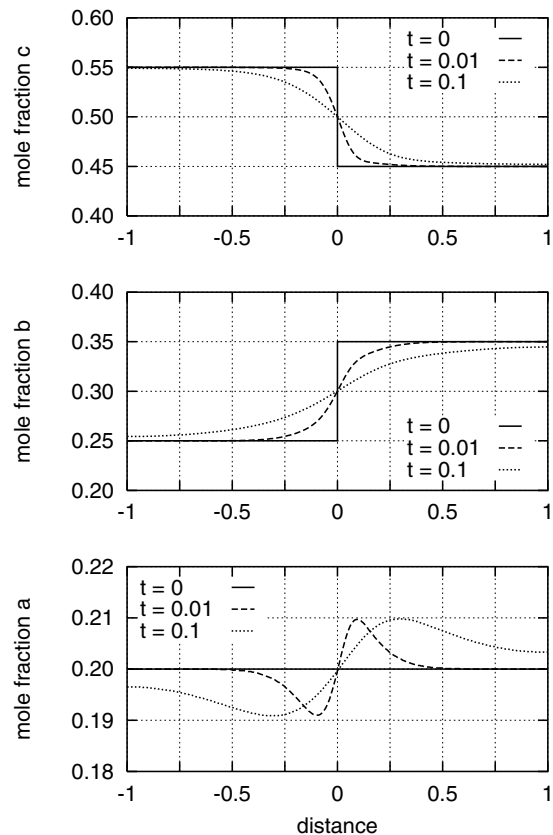


Fig. 2. Model diffusional profiles at different times in an ideal ternary solution. Uphill diffusion can clearly be observed in the a component together with a slight degree of asymmetry. Arbitrary time and distance units have been used and zero-flux boundary conditions have been imposed. Component c is taken as the dependent component, with values for the mobilities of $M_{aa} = 1$, $M_{ab} = -0.5$, $M_{ba} = -0.5$, and $M_{bb} = 1$.

convergence. Such instabilities are a consequence of the inherent non-linearity of the L coefficients.

In the spectral collocation numerical scheme, Chebyshev polynomials were chosen as the basis functions and the residual function was minimized at the collocation points of the Chebyshev–Gauss–Lobatto mesh. The physical space was divided into two equal subdomains to obtain a higher density of points in the interfacial region where the concentration gradients are steepest. The solution of the equations was then approximated on each subdomain by Chebyshev polynomials of order 48. The solutions over the two subdomains were matched at the common interface by imposing continuity of the approximating functions and their first derivatives. The scheme was implemented using the MATLAB® programming environment. Interestingly, this numerical solution scheme produced stable results over a wider range of initial conditions and model parameters than the finite element method. Alternative strategies that may further increase the accuracy and stability of the solutions are currently being explored.

The difference between the solutions obtained using the two schemes was minimal. In this section, the results from the finite element method are presented. The initial conditions were defined by splitting the domain into two equal subdomains containing different concentrations of components and solutions were obtained for zero-flux boundary conditions.

Model diffusional profiles obtained by solving (17)–(19) with $\chi = 0$ demonstrate that uphill diffusion can occur given certain values of M , even in ideal ternary solutions (Fig. 2), and such behavior is in agreement with that predicted by Cooper [32] and Nishiyama [15]. Furthermore, it can be seen that while the position of the “uphill” concentration peak shifts with time, the magnitude does not change significantly, reflecting the relatively long time required for the complete relaxation of the phenomenon. Significantly, the profiles produced during the simulations strongly resemble those of reported experimental diffusion couples [3–5,8,21].

Due to the complexity of the equations, a systematic parametric analysis was found to be of limited use in assessing the influence of the different model parameters.

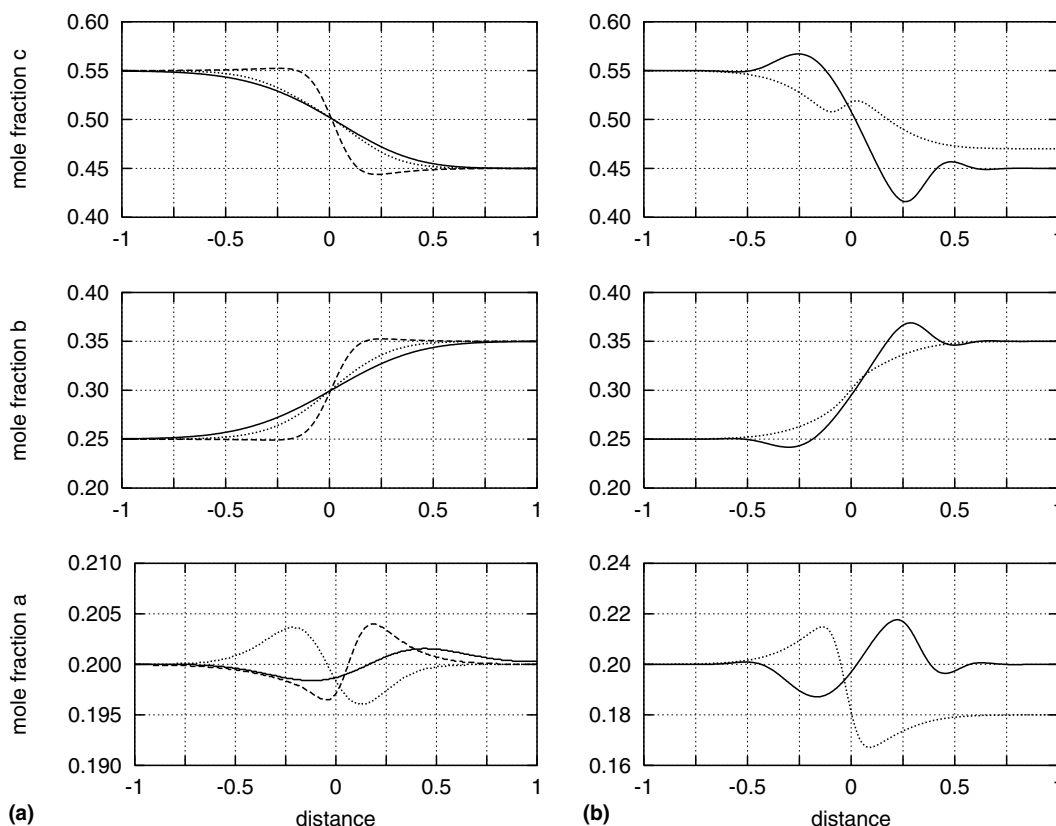


Fig. 3. (a) Model diffusional profiles for an ideal solution demonstrating pronounced off-center asymmetry. The solid line represents values of $M_{aa} = 1$, $M_{ab} = 0.5$, $M_{ba} = 0.5$, and $M_{bb} = 1$ and the dashed line values of $M_{aa} = 1$, $M_{ab} = 0.5$, $M_{ba} = 0.5$, and $M_{bb} = 0.3$ ($t = 0.1$). The dotted profile shows the reversal of the uphill trend with values for the mobility parameters of $M_{aa} = 0.5$, $M_{ab} = 0.5$, $M_{ba} = 0.5$, and $M_{bb} = 1$ ($t = 0.05$). The initial conditions are the same as those for Fig. 2. (b) Model diffusional profiles for an ideal solution demonstrating second order features. The solid line represents mobility values of $M_{aa} = 2$, $M_{ab} = -1$, $M_{ba} = 3$, and $M_{bb} = 1$ ($t = 0.01$) with the initial conditions of Fig. 2. The dotted line shows calculated profiles for mobility values of $M_{aa} = 0.9$, $M_{ab} = 0.5$, $M_{ba} = 0.5$, and $M_{bb} = 0.1$ ($t = 0.05$) with initial conditions of $\phi_a(-1 < x \leq 0) = 0.2$, $\phi_b(-1 < x \leq 0) = 0.25$, $\phi_a(0 < x < 1) = 0.18$, $\phi_b(0 < x < 1) = 0.35$.

Instead, a discussion of the features that the equations can produce demonstrates the potential for the free energy model to account for some of the complex behavior observed in experimental systems.

While near symmetric behavior can be observed in Fig. 2, one of the interesting features of the model is its ability to produce markedly asymmetric profiles. Although asymmetry in both the centers of concentration peaks and their magnitude are sometimes observed in experiments, e.g. [8,21], the D matrix model is unable to reproduce such behavior. As a result, such observations have typically been attributed to experimental error. In Fig. 3(a), pronounced off-center uphill diffusion profiles can be observed for certain values of M , with a reversal in the trend being produced by changing the mobility parameters. Furthermore, in addition to a high degree of asymmetry, second order features can also be produced with certain initial conditions and values of M (Fig. 3(b)). Clearly, uphill diffusion and the development of second order features, such as those visible in Fig. 3, are also dependent on the initial concentration steps. Significantly, in an experimental study of silicate melts, Kress and Ghiorso [21] con-

cluded that the discrepancies between the D matrix model and the complex second order features observed in their experiments suggested that alternative models were required.

When solving (17)–(19) for $\chi \neq 0$, it can be seen that the non-ideality χ parameters also have a significant effect on the diffusional profiles (Fig. 4). However, generalizations concerning the overall influence of χ are difficult to make primarily because χ can act so as to enhance or suppress uphill diffusion and asymmetric behavior. Specifically, for the initial conditions and values of M examined in Fig. 4(a), the greatest level of enhancement occurs for $\chi_{ac} = 2$ and $\chi_{bc} = -2$, while the greatest level of “suppression” occurs at $\chi_{ac} = -2$ and $\chi_{bc} = 2$. However, for the different initial conditions examined in Fig. 4(b), the most asymmetric features, similar to those reported by [33], are obtained for $\chi_{ac} = -2$ and $\chi_{bc} = 2$. The physical meaning associated with positive and negative values of χ was discussed following (15).

As evident from the examples presented in this section, the free energy model has the ability to accurately capture a wide range of experimentally observed be-

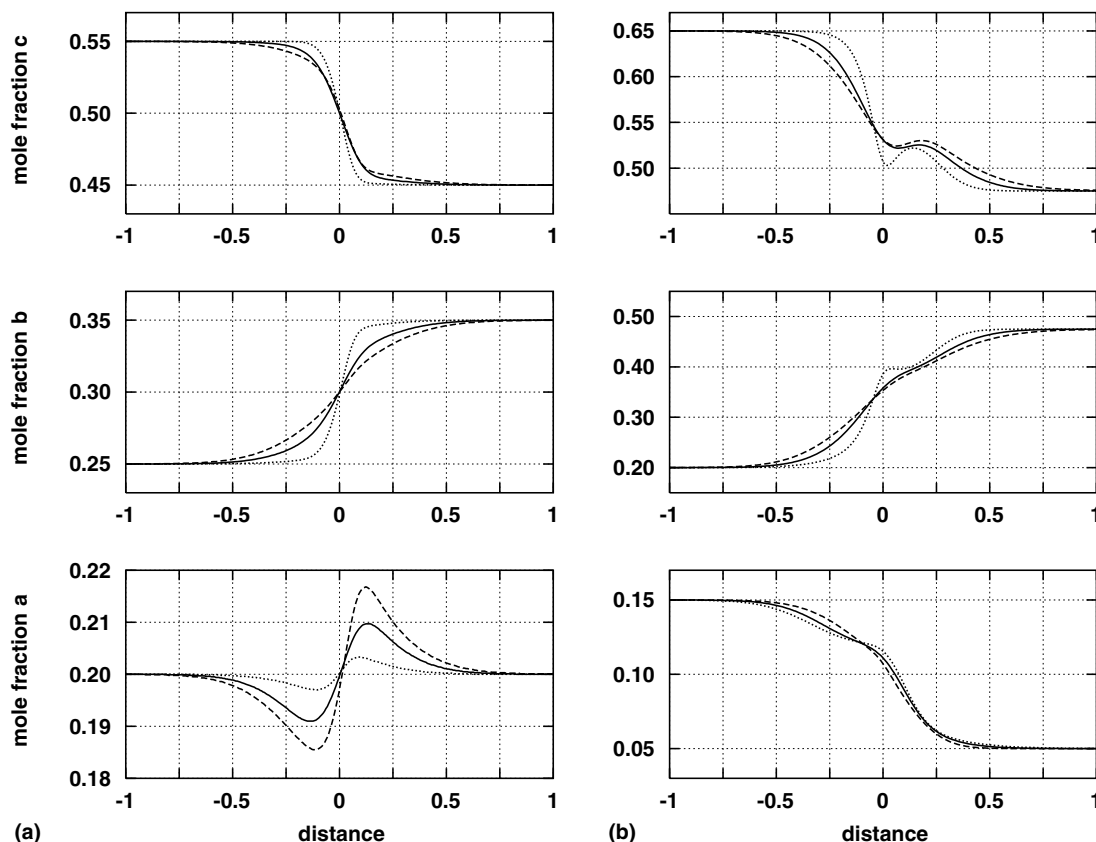


Fig. 4. Model diffusional profiles for different values of χ . The solid lines represent ideal solutions (i.e. $\chi_{ac} = 0$ and $\chi_{bc} = 0$), the dashed lines indicate profiles for $\chi_{ac} = 2$ and $\chi_{bc} = -2$, and the dotted lines represent diffusion for $\chi_{ac} = -2$ and $\chi_{bc} = 2$. (a) Initial and boundary conditions, as well as the values for the mobility parameters, are the same as those for Fig. 2 ($t = 0.02$). (b) Initial conditions are given by $\phi_a(-1 < x \leq 0) = 0.15$, $\phi_b(-1 < x \leq 0) = 0.2$, $\phi_a(0 < x < 1) = 0.05$, $\phi_b(0 < x < 1) = 0.475$.

havior in ternary systems. Furthermore, the model is able to produce diffusional profiles that cannot be reproduced by the simpler Fickian approach of the D matrix model.

While we stress that the free energy model is local in space and time, we do not exclude the possibility that the inherent disorder of certain systems can introduce memory effects in the profiles. In order to incorporate such effects into the free energy model, an approach similar to that suggested by Dentz et al. [34] could be adopted. This model is based on the Continuous Time Random Walk (CTRW) theory and introduces a time memory function, $\mathcal{M}(t)$. The equations to describe a ternary system can be expressed concisely as a convolution in time of the memory function and the divergence of the flux

$$\frac{\partial \phi_a}{\partial t} = - \int_0^t dt' \mathcal{M}_a(t-t') \nabla \cdot J_a(t'), \quad (20a)$$

$$\frac{\partial \phi_b}{\partial t} = - \int_0^t dt' \mathcal{M}_b(t-t') \nabla \cdot J_b(t'). \quad (20b)$$

For a detailed account of the CTRW theory, the interested reader is referred to [34] and references therein.

In the next section, a direct comparison of the free energy model in (17)–(19) with data from specific silicate systems will be explored.

4. Comparison with experimental data

Examination of experimental data serves two main purposes in the present study: (1) to test the ability of the free energy model to fit specific experimental data, and (2) to constrain the M and χ parameters in a real system. Before proceeding, it is useful to briefly review the criteria demanded of experimental data for a meaningful comparison between theory and experimental results.

Although ternary diffusion has been explored in a variety of systems, it is convenient to study data from silicate melts and glasses as detailed concentration profiles have been reported in numerous studies. Typically,

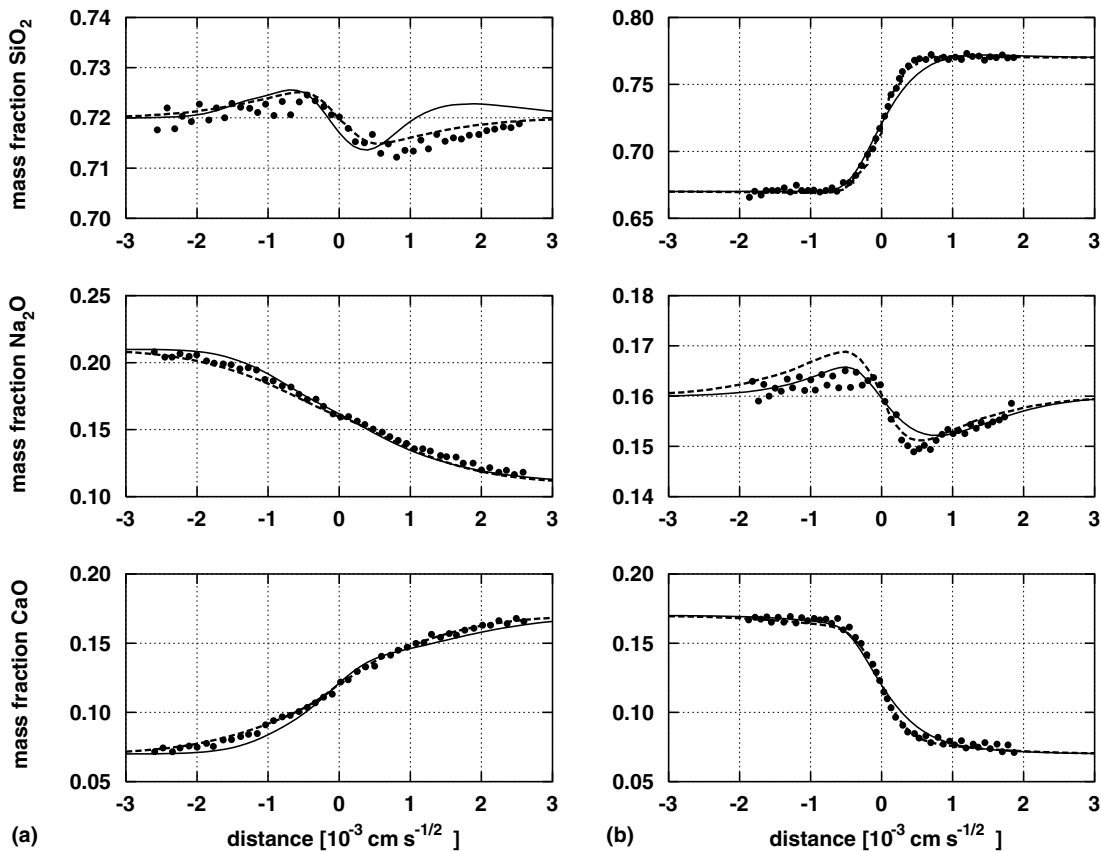


Fig. 5. Comparison of the free energy model profiles (solid lines) with experimental data (points) from two different diffusion couples reported by Wakabayashi and Oishi [4]. The best fit for the D matrix model is also shown (dashed lines). Setting SiO_2 as the dependent component, an error minimization technique produced the following free energy model parameters: $M_{\text{CaO-CaO}} = 3.63 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $M_{\text{CaO-Na}_2\text{O}} = -3.38 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $M_{\text{Na}_2\text{O-CaO}} = 3.28 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $M_{\text{Na}_2\text{O-Na}_2\text{O}} = 3.59 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $\chi_{\text{CaO-SiO}_2} = 3.21$, and $\chi_{\text{Na}_2\text{O-SiO}_2} = 3.01$. By comparison, the D matrix model parameters are $D_{\text{CaO-CaO}} = 2.82 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{CaO-Na}_2\text{O}} = -6.52 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{Na}_2\text{O-CaO}} = -2.81 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $D_{\text{Na}_2\text{O-Na}_2\text{O}} = 8.14 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

such diffusion experiments involve the preparation of a diffusion couple consisting of two initially homogeneous glasses of different compositions. After heating for a certain length of time, the couple is quenched and the compositional profiles measured. In order to reliably fit the D matrix model to experimental data for ternary systems, at least two independent experiments are required in which the compositions of the two couples differ significantly [22].

As an additional two parameters are introduced in the free energy model, a third experiment is ideally required in order to accurately constrain the M and χ parameters. While a number of different studies have reported data concerning diffusion couples in silica melts, the dataset from Wakabayashi and Oishi [4], describing diffusion couples in $\text{CaO-Na}_2\text{O-SiO}_2$ melts at 1500 °C, was found to be the most suitable for the purposes of the present study. Although only two profiles were available in the dataset, the initial conditions produced relatively stable configurations for the calculation of the profiles.

By coupling the spectral collocation method described in the previous section with an error minimization technique that simultaneously determined the error on two digitized datasets, values for M and χ were obtained. In calculating the profiles, differences in the molar masses of the components have not been accounted for, and this simplification implies that mass and molar fluxes are interchangeable. Results of the application of the minimization technique to the data of [4] can be seen in Fig. 5 together with the D matrix model profiles. Values for the model parameters are reported in the caption to Fig. 5. It can be seen that there is a satisfactory agreement between the free energy model and the experimental data, comparable to that of the best fit obtained with the D matrix model. It is expected that the level of agreement between the data and the free energy model will be further improved when the numerical instability difficulties inherent in applying the model are resolved.

Consideration of the free energy model in the context of these experiments highlights the potential of this model to contribute to a fuller physical understanding of diffusional processes. For example, the magnitude of the “mutual” mobility parameters, M_{ab} and M_{ba} , is similar to that of the “intrinsic” mobility parameters, M_{aa} and M_{bb} , suggesting that cross diffusion in this system is a process that is equally important in determining the diffusion of both components. Such a conclusion cannot be drawn from an examination of the D coefficients. Furthermore, the positive values obtained for the χ parameters imply that the excess free energies of mixing for both the CaO-SiO_2 and $\text{Na}_2\text{O-SiO}_2$ systems are also positive, and therefore endothermic processes. Importantly, the magnitudes of these parameters retrieved from the minimization procedure are physically reasonable.

5. Discussion

From the numerical analysis and comparison with experimental data presented here, it can be seen that the free energy model is capable of describing many of the expected diffusional features in ternary systems. Nevertheless, several issues relating to the application of the model must be recognized and they will be discussed below.

One obvious theoretical uncertainty concerns the possible influence of concentration on the mobility and χ parameters. While these parameters might be expected to be less affected by concentration than diffusion coefficients, it remains possible that compositional dependence may account for at least some of the differences observed between the model and experimental data. The choice of function used to describe the free energy of the system could also require reexamination. Although convenient, the Simple Mixture model may not accurately describe the system and more complex expressions for the free energy, such as the Margules equation [28], might be required.

As mentioned above, numerical instabilities were observed for certain combinations of parameters and initial conditions. When attempting to minimize the error with respect to experimental data, “unstable” combinations of parameters are disregarded despite the possibility that they may be physically feasible and could even provide good fits. Furthermore, even if a numerical algorithm is capable of successfully evaluating every possible combination of parameters, standard minimization techniques are likely to have difficulty in successfully finding the optimal combination for the six parameters. Thus, the successful resolution of these numerical difficulties is clearly an important future step.

In addition to the numerical difficulties, another challenge is posed by the intrinsic uncertainty associated with experimental systems. Even relatively small experimental errors may make it difficult to reliably retrieve model parameters, and while a number of precise experimental studies have been published examining diffusion in ternary systems, continued improvements in analytical techniques are likely to reduce experimental error even further. In addition, improved experimental design might also help to determine conclusively whether or not the asymmetric features sometimes noted in concentration profiles are diffusional or density related phenomena [35].

6. Conclusions

This study proposes a set of coupled non-linear equations describing diffusion in ternary systems based on a free energy approach. These equations have been solved for 1D configurations and compared to experimental

data. The model was found to be successful in capturing much of the qualitative and quantitative behavior of multicomponent systems. Unlike current models, the free energy approach reproduces asymmetry and second order features observed in experiments. Furthermore, the parameters in the diffusion equations representing the enthalpic contribution to the free energy can be measured in independent thermodynamic experiments. Currently being explored is the application of the equations to more comprehensive datasets and the examination of alternative functions for the free energy of mixing. Future improvements in both computational and experimental methods are likely to be the key towards a more complete understanding of diffusion in multicomponent systems.

Acknowledgements

The authors thank the Marie Curie Individual Fellowship Programme (A.C.) and British Petroleum International for financial support (S.E. and B.B.).

Appendix A

The chemical potential of component a in a ternary single-phase system is given by [25]

$$\mu_a = G^{\text{mix}} - \phi_b \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} - \phi_c \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b}, \quad (\text{A.1})$$

where the chemical potential has been normalized by RT . The gradient of the chemical potential may be written as

$$\begin{aligned} \nabla \mu_a = \nabla G^{\text{mix}} - \nabla \left[\phi_b \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} \right] \\ - \nabla \left[\phi_c \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b} \right] \end{aligned} \quad (\text{A.2})$$

and the expression may be expanded to obtain

$$\begin{aligned} \nabla \mu_a = \nabla G^{\text{mix}} - \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} \nabla \phi_b \\ - \phi_b \nabla \left[\left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} \right] - \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b} \nabla \phi_c \\ - \phi_c \nabla \left[\left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b} \right]. \end{aligned} \quad (\text{A.3})$$

From the chain rule, the gradient of the free energy of mixing is equal to

$$\nabla G^{\text{mix}} = \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} \nabla \phi_b + \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b} \nabla \phi_c \quad (\text{A.4})$$

and (A.1) thus simplifies to

$$\nabla \mu_a = -\phi_b \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_b} \right)_{\phi_c} - \phi_c \nabla \left(\frac{\partial G^{\text{mix}}}{\partial \phi_c} \right)_{\phi_b}. \quad (\text{A.5})$$

Clearly, similar expressions can be obtained for the other components in the system.

References

- [1] H.L. Toor, *AIChE J.* 3 (1957) 198.
- [2] Y. Oishi, M. Nanba, J.A. Pask, *J. Am. Ceram. Soc.* 65 (1982) 247.
- [3] A.K. Varsheneya, A.R. Cooper, *J. Am. Ceram. Soc.* 55 (1972) 312.
- [4] H. Wakabayashi, Y. Oishi, *J. Chem. Phys.* 68 (1978) 2046.
- [5] E.B. Watson, *Contrib. Mineral. Petrol.* 56 (1982) 73.
- [6] S. Chakraborty, D.B. Dingwell, D.C. Ruble, *Geochim. Cosmochim. Acta* 59 (1995) 255.
- [7] S. Chakraborty, D.B. Dingwell, D.C. Rubie, *Geochim. Cosmochim. Acta* 59 (1995) 265.
- [8] Y. Liang, F.M. Richter, E.B. Watson, *Geochim. Cosmochim. Acta* 60 (1996) 5021.
- [9] H. Sato, *Contrib. Mineral. Petrol.* 50 (1975) 49.
- [10] Y. Zhang, D. Walker, C.E. Lesher, *Contrib. Mineral. Petrol.* 102 (1989) 492.
- [11] J.P. Davidson, S.L. Desilva, P. Holden, A.N. Halliday, *J. Geophys. Res.* 95 (1990) 17661.
- [12] A. Acosta-Vigil, D. London, T.A. Dewers, G. Morgan, *J. Petrol.* 43 (2002) 1885.
- [13] Y. Oishi, *J. Chem. Phys.* 43 (1965) 1611.
- [14] D.G. Miller, *J. Phys. Chem.* 63 (1959) 570.
- [15] T. Nishiyama, *Phys. Earth Planetary Interiors* 107 (1998) 33.
- [16] Y. Zhang, *J. Geophys. Res.* 98 (1993) 11901.
- [17] R. Krishna, J.A. Wesselingh, *Chem. Eng. Sci.* 52 (1997) 861.
- [18] M.A. Dayananda, C.W. Kim, *Metall. Trans. A* 10 (1979) 1333.
- [19] P.K. Gupta, A.R. Cooper, *Physica* 54 (1972) 39.
- [20] S.R. de Groot, P. Mazur, *Non-equilibrium Thermodynamics*, second ed., Dover, New York, 1982.
- [21] V.C. Kress, M.S. Ghiorso, *Geochim. Cosmochim. Acta* 57 (1993) 4453.
- [22] A.F. Trial, F.J. Spera, *Geochim. Cosmochim. Acta* 58 (1994) 3769.
- [23] J.W. Cahn, J.E. Hilliard, *J. Chem. Phys.* 28 (1958) 258.
- [24] E.B. Nauman, D.Q. He, *Chem. Eng. Sci.* 56 (2001) 1999.
- [25] H.C. Van Ness, M.M. Abbott, *Classical Thermodynamics of Non-electrolyte Solutions*, McGraw-Hill, New York, 1982.
- [26] D.D. Fitts, *Nonequilibrium Thermodynamics*, McGraw-Hill, New York, 1962.
- [27] G.N. Lewis, M. Randall, *Thermodynamics*, second ed., McGraw-Hill, New York, 1961.
- [28] G. Ganguly, S. Saxena, *Mixtures and Mineral Reaction*, Springer, Berlin, 1987.
- [29] S. Chakraborty, *J. Phys. Chem.* 98 (1994) 4923.
- [30] J.P. Boyd, *Chebyshev and Fourier Spectral Methods*, second ed., Dover, New York, 2000.
- [31] L.N. Trefethen, *Spectral Methods in MATLAB*, SIAM, Philadelphia, PA, 2000.
- [32] A.R. Cooper, in: A. Hofmann, B. Giletti, R. Yund (Eds.), *Geochemical Transport Kinetics*, Carnegie Institution of Washington, 1974, p. 15.
- [33] Y.H. Sohn, M.A. Dayananda, *Acta Mater.* 48 (2000) 1427.
- [34] M. Dentz, A. Cortis, H. Scher, B. Berkowitz, *Adv. Water Resour.* 27 (2) (2004) 173, doi:10.1016/j.advwatres.2003.11.002.
- [35] Y. Liang, F.M. Richter, E.B. Watson, *Nature* 369 (1994) 390.